Storage and export of mercury from a contaminated bay (Ria de Aveiro, Portugal)

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Abstract

Mercury has been determined in water, suspended particulate matter (SPM) and sediments (solid fraction and pore water) collected in a heavily contaminated confined area (Largo do Laranjo) of the Ria de Aveiro. Mercury has been analysed in seabass (*Dicentrarchus labrax*) captured in several locations of the lagoon. The levels of mercury in water and SPM in the contaminated sampled places fluctuated daily with the tide (from 10 to 53 ng.dm^{-3} and 3.5 to 26 μg.g^{-1}, respectively), indicating the export at the tidal rhythm. Bottom sediments exhibited higher concentrations, the maximum (48 μg.g^{-1}) occurring near the anthropogenic source at depths corresponding to the periods of higher industrial discharges. Mercury concentrations in pore waters (max. 80 ng.dm^{-3}) exceed the values found in the water column and were higher at depths where Acid Volatile Sulphides (AVS) presented broad maximums. This implies a remobilization at anoxic conditions. However the export across the sediment-water interface predicted through molecular diffusion is low (between 1 to 4 $\times$ 10^{-3} ng.cm^{-2}.h^{-1}) in comparison to the industrial input. The anthropogenic mercury appears to be rapidly accumulated in seabass, a predator fish that enter seasonally in Largo do Laranjo.

Introduction

Mercury has been identified as a major pollutant in a few confined bodies of the coastal zone (Cossa and Martin, 1991; Kudo and Miyhara, 1992; Mason et al., 1998; 1999). Due to its acute toxicity the understanding of the biogeochemical dynamics is, thus, considered of great importance in these ecosystems (Cossa et al., 1988; Bacci, 1989; Kudo and Miyahara, 1992). In general, mercury in the aquatic environment tends to be associated with suspended particles and is scavenged from the water column to bottom sediments (Wallmann et al., 1996; Lee et al., 1998). Sediments may function as repository of anthropogenic mercury (Ravichandran et al., 1995) or as internal sources when mercury is released to pore water (Arakel, 1995; May et al., 1997). Transfer of mercury to the water column may deleteriously affect the biota (Watras and Bloom, 1992; Becher and Bigham, 1995; Morgan and Mason, 1997).

Ria de Aveiro is a coastal lagoon connected to the sea through a single artificially maintenance entrance. The lagoon is located in the north-western coast of Portugal and covers an area of 43 km^2 at low tide with islands and channels that originate a complex circulation of water and particles. During more than four decades a chlor-alkali industry discharged an effluent rich in mercury in a remote branch of the lagoon that ends in a bay, Largo do Laranjo (Figure 1). In the last decade, the industry changed their technology and the discharge of anthropogenic mercury diminished considerably (Pereira, 1997). However, mercury concentration in surface sediments of Largo do Laranjo, between 2.3 and 63 μg.g^{-1} (Pereira, 1997), are much higher than pre-industrial levels (0.05 μg.g^{-1}; Laane, 1992). Due to the severe contamination with mercury, several works have been carried out in Ria de Aveiro related to sediments (Lucas et al., 1986; Hall et al., 1987; Pereira, 1997; Pereira et al., 1997; 1998a), wa-

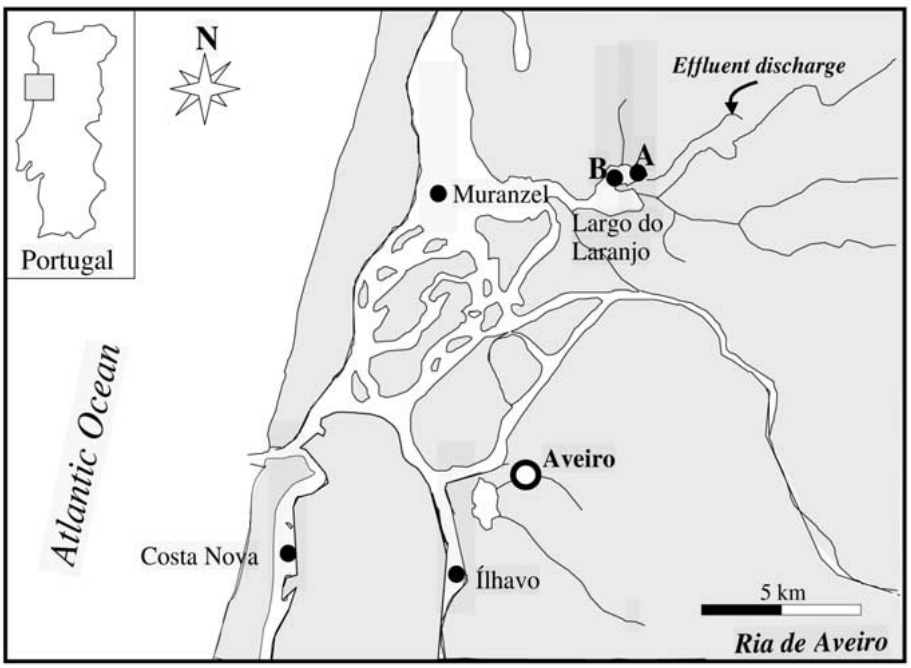

Figure 1. Map of Ria de Aveiro and sampling sites – Largo do Laranjo (stations A and B) and Muranzel, Costa Nova and Ílhavo.

ter (Pereira et al., 1995; 1998b) and organisms (Lima, 1986; Lucas et al., 1986; Abreu et al., 1999). The understanding of mercury mobility in sediments and the present availability to living organisms are crucial for a successful remediation of contaminated areas.

This work examines the distribution of mercury in sediment cores and pore waters from the most contaminated area of the Ria de Aveiro, its remobilization to the water column and the accumulation in seabass caught at different sites in the region.

Material and methods

Samples collection and treatment

Two tidal mud depositional areas in Largo do Laranjo were selected for study (Figure 1, stations A and B). Water samples and sediment cores were collected in April 1997. Sediments were sampled using hand-held PVC acid-cleaned tubes, transported vertically to the laboratory, sampled the topmost surface sediments (0–5 mm layer), and sectioned at 5-cm depth intervals in a nitrogen-filled glove bag to prevent oxidation reactions within the anaerobic sediment (Wallmann et al., 1996). Sediment sub-samples were stored at –20 °C. Seabass fish samples (*Dicentrarchus labrax*) of about 20-cm length were caught in Largo do Laranjo, Muranzel, Costa Nova and Ílhavo along the Ria de Aveiro (Figure 1).

Waters samples were immediately filtered in the laboratory through 0.45 μm Millipore (HA) filters. The dissolved fraction was acidified to pH<2 with HNO_3 (conc., 'mercury-free') and maintained at 4 °C until analyses. The particulate matter retained in the filters were oven dried at 70 °C during one night. Pore waters samples were extracted from sediments at each sampling depth interval under nitrogen atmosphere, by centrifugation at 6,000 rpm, during 20 minutes (B. Braun, model Sigma 4–10). The supernatant was filtered through Millipore (HA) filters of 0.45 μm and the filtrate was collected in acid-cleaned polyethylene bottles, preserved by acidification to pH<2 with HNO_3 (conc., 'mercury-free') and placed at 4 °C. A similar volume of ultrapure water was carried through the centrifugation and filtration procedure as a blank procedure. After homogenisation, 0.5 to 1 g subsamples of all dry sediments were treated with HNO_3 and HCl (Pereira et al., 1995). Total mercury was measured in the digest. Subsamples of the sediment cores were also taken for analysis of Acid Volatile Sulphide (AVS) according to the procedure described by Casas and Crecelius (1994). The fishes were dissected and muscle tissue samples separated, weighted

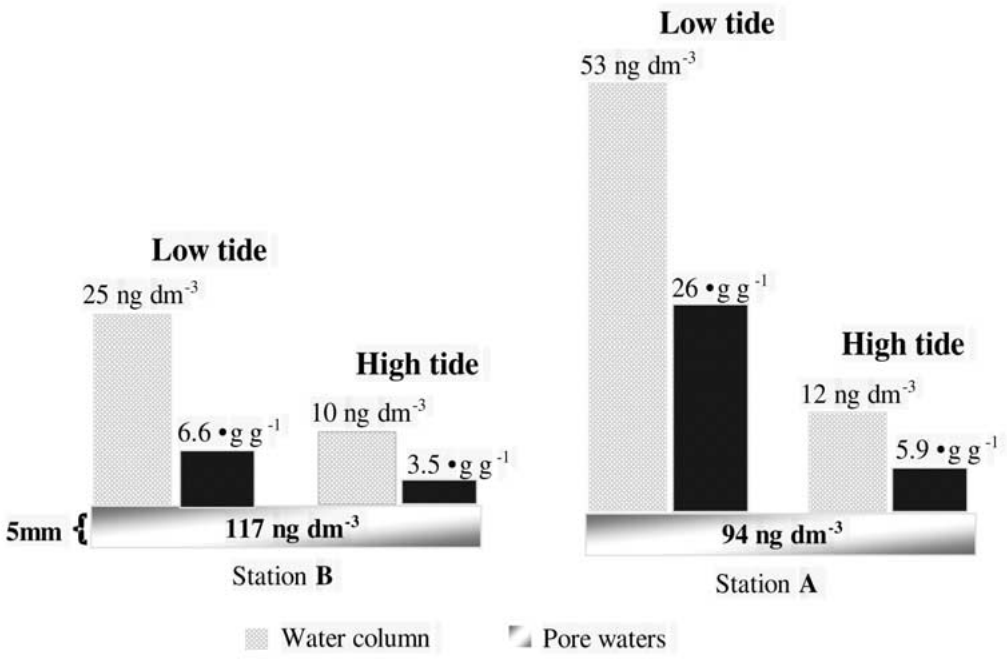

Figure 2. Reactive dissolved mercury in water column (ng dm^{-3}) and total mercury concentrations in suspended particulate matter ($\mu g\ g^{-1}$) at low and high tide and reactive dissolved mercury in pore waters in stations A and B.

and freeze dried; the dry weight/fresh weight ratio was established. Mineralization of samples was performed according to the methodology described by Sadiq et al. (1991).

Samples analysis

All chemical measurements included analysis of duplicates and blanks. Filtered pore waters and water samples were analysed for reactive mercury by cold vapour atomic fluorescence spectrometry (cold vapour generator PSA, model 10.003, associated to a detector Merlin PSA model 10.023). Mercury determination on sediment and muscle fish tissue digests was performed by a gold amalgamation pre-concentration procedure, thermal desorption and cold vapour atomic absorption spectrophotometry (Perkin Elmer, model 3030B associated to an MHS-20 system). The concentration of total mercury in sediment standard (PACS-2, 3.04 $\pm$ 0.20 $\mu g.g^{-1}$, mean and standard deviation) was within the reference values (3.05 $\mu g.g^{-1}$, n = 12). Total mercury determinations in certified fish tissues (CRM 463 – tuna fish, 2.85 0.16 $g.g^{-1}$) also do not differ significantly at 95% confidence level of the reference values (2.70 0.07 $g.g^{-1}$, n = 25). The relative standard deviation of mercury measurements in the digests was always $< 6\%$ (n = 6) and $< 10\%$ for reactive dissolved mercury determinations (n = 4).

Results

Mercury in water column

Dissolved reactive mercury in the water column varied daily between low and high tide. Concentrations at stations A and B were 53 and 25 $ng.dm^{-3}$ at low tide and 10 and 12 $ng.dm^{-3}$ at high tide, respectively (Figure 2). Alterations with the tide were also found in total particulate mercury: 26.0 and 6.6 $\mu g\ g^{-1}$ at low tide and 5.9 and 3.5 $\mu g\ g^{-1}$ at high tide for stations A and B. Broader intervals of both dissolved and particulate concentrations were observed at station A, located near Estarreja channel where the industrial mercury is discharged.

Mercury in solids and sediment pore waters

Total mercury concentrations in sediment cores collected at stations A and B are shown in Figure 3. The vertical profile obtained for the two stations is characterised by a maximum below the surface. The peak values were found at 23 cm depth (48 $\mu g.g^{-1}$

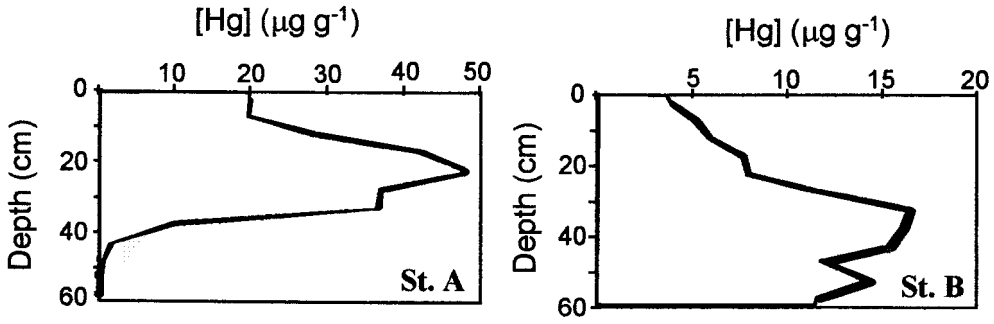

Figure 3. Vertical distribution of total mercury concentrations (μg g^{-1}) in sediments from stations A and B.

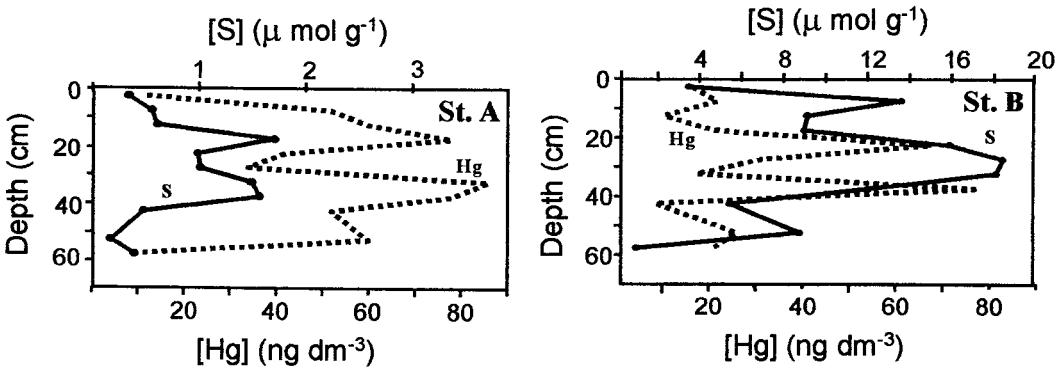

Figure 4. Vertical distribution of reactive dissolved mercury (ng dm^{-3}) in pore waters and AVS (μmol dm^{-3}) concentrations in sediments from stations A and B.

Table 1. Total mercury concentration (μg.g^{-1}, fresh weight; mean and standard deviation) in seabass (*Dicentrarchus labrax*) muscle (n between 7 and 17).

Largo do Laranjo	Muranzel	Ílhavo	Costa Nova
1.1 ± 0.02	0.45 ± 0.03	0.15 ± 0.02	0.11 ± 0.02

at station A) and at 33 cm (17 μg.g^{-1} at station B). Surface concentrations were about 20 μg.g^{-1} at station A and 4 μg.g^{-1} at station B. Background values (0.05 μg.g^{-1}) were recorded at 58-cm depth at station A.

Reactive mercury concentrations in pore waters showed two maximum (around 80 ng.dm^{-3}) approximately at 20 and 35 cm depth (Figure 4). Pore water concentrations are not correlated to mercury concentrations in the solids, but peaks occur at depths of higher AVS values.

Mercury in seabass muscle

Total mercury concentrations in seabass varied with site (Table 1). Higher mercury residues were found in specimens caught inside the contaminated bay (1.1 μg.g^{-1}, fresh weight) in clear contrast to values found in individuals from other areas of the lagoon (0.11–0.45 μg.g^{-1}, fresh weight).

Discussion

Mercury concentrations in the lagoon are greatly influenced by the industrial discharge into Largo do Laranjo (Pereira et al., 1998a). Although contamination levels have decreased as the effluent treatment was implemented in 1994 (Pereira, 1997) differences in mercury concentrations in Laranjo at low and high tide indicates the ongoing discharge of industrial mercury to the ecosystem. However, the tide appears to have a major dilution effect inside the lagoon, and therefore concentrations fluctuate with the water volume.

Sediments in Largo do Laranjo are heavily contaminated with mercury and the depth variation reflect

the industrial discharges evolution during the last decades. Previous works at several locations of the area confirm that the peak concentrations are associated with periods of higher industrial production (Pereira et al., 1998a). In spite of the storage capacity of the sediments, pore water profiles indicate that mercury is remobilized in anoxic sediments. This is an important geochemical and toxicological aspect (Wallmann et al., 1996). Maximum of dissolved and particulate mercury at different sediment layers in Largo do Laranjo implies that mercury concentrations in pore waters are not entirely controlled by exchange equilibrium between the solid phase and pore waters. Moreover, the high concentrations of mercury in pore water suggest that HgS precipitation is not limiting its solubility. The formation of polysulphide as well as organic complexes, has been suggested to explain the presence of pore water metal concentrations in larger values than those predicted by the thermodynamic solubility of metal sulphide, HgS (Gagnon et al., 1997). The complexes with polysulphide species may dominate in sulphidic estuarine waters (Dyrssen, 1985; Paquette and Helz, 1995). Such an explanation could be valid to the mercury pore water profiles observed in our study area.

Because concentrations in pore waters exceeded values in water column it should be assessed whether sediments are important internal sources of mercury to the water column. On the basis of the values presented in Figure 2 the predicted diffusive fluxes may be calculated according to Fick's first law of diffusion (Berner, 1980). Using values of diffusion coefficient refereed in Wallmann et al. (1996) and Gagnon et al. (1997) and a mean porosity of 0.8, the estimated fluxes ranged from 1 to 4×10^{-3} ng.cm^{-2}.h^{-1}. These quantities are extremely low in comparison to the industrial discharged, as referred in Pereira (1997) and as it can be inferred from the values of reactive dissolved mercury at low tide (Figure 2). Therefore, diffusive fluxes are not sufficiently high to influence substantially the water column mercury concentrations. However, it should not be minimised the importance of advective processes related to tidal excursion and wind. In a previous work (Pereira et al., 1998b) it has been found that bottom erosion, occurring in periods of stronger tidal currents, results in the resuspension and escape of particulate mercury.

Higher residues of mercury in seabass caught in Laranjo basin points out to the present ecological effect of mercury contamination. Although industrial discharges have decreased considerably in past five years (Pereira, 1997) and sediments act mainly as a repository of mercury, seabass that enter the area became contaminated with mercury. Further ongoing studies attempt to clarify the transfer of mercury across the web food chain.

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